

*Recombination of Ions at Different Temperatures.*

By P. PHILLIPS, D.Sc., B.A., Royal Veterinary College, Camden Town.

(Communicated by Prof. F. T. Trouton, F.R.S. Received November 10, 1909,—  
Read January 13, 1910.)

Doubts were felt about the results of McClung's experiments on this subject very soon after he published them, and Langevin indicated the weak point in them by showing that, in the apparatus used, diffusion would have a large effect and would be responsible at the higher temperatures for most of the disappearance of the ions. The present experiment was therefore carried out under such conditions that the diffusion could be safely neglected. At the highest temperature attained it will be seen that the diffusion is probably not quite negligible, but the error even here is certainly not a very large fraction of the whole.

*Theory of the Method.*

A layer of air of uniform thickness situated between two parallel electrodes is ionised by a single flash from a Röntgen bulb. The quantity of electricity received by either electrode will depend upon the field established between them. It is easy to show that

$$N = \frac{(k_1 + k_2) X}{\alpha} \log \left( 1 + \frac{\alpha n_0 t}{(k_1 + k_2) X} \right),$$

where  $N$  is number of ions received per unit area of the electrode;  $k_1$  and  $k_2$  are the velocities in unit field of the positive and negative ions respectively;  $X$  is the field;  $\alpha$  is the coefficient of recombination;  $n_0$  is number of ions per cubic centimetre originally produced by the flash;  $t$  is thickness of the layer of air ionised.

If, therefore, the number of ions received per square centimetre is  $N_1$  when the field is  $X_1$  and  $N_2$  when the field is  $X_2$ , then

$$\frac{N_1 - N_2}{N_1} = 1 - \frac{X_2}{X_1} \log \left( 1 + \frac{\alpha n_0 t}{(k_1 + k_2) X_2} \right) \bigg/ \log \left( 1 + \frac{\alpha n_0 t}{(k_1 + k_2) X_1} \right).$$

This experiment measures  $(N_1 - N_2)/N_1$ , a deflection  $D_0$  which is proportional to  $n_0$ , and the differences of potential  $V_2$  and  $V_1$  between the electrodes which are proportional to the fields  $X_2$  and  $X_1$ .

Let  $n_0 = a D_0$ ,

$X_2$  and  $X_1 = bV_2$  and  $bV_1$  respectively,

$a$  and  $b$  being constants.

Throughout this experiment  $V_1 = 100$  volts and  $V_2 = 20$  volts and therefore the equation becomes

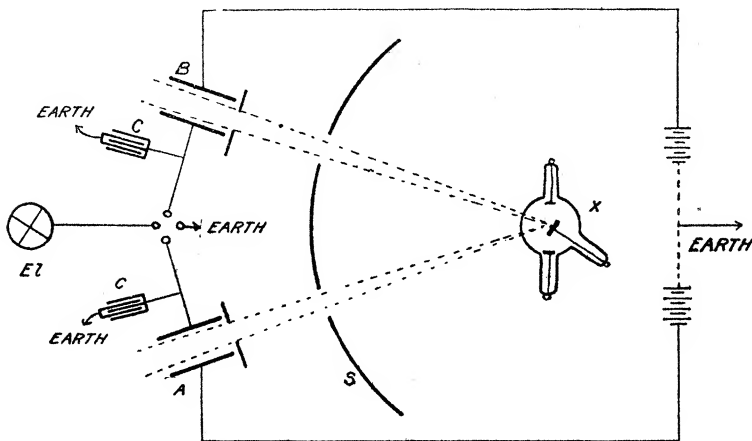
$$\frac{N_1 - N_2}{N_1} = 1 - \frac{1}{5} \log \left( 1 + \frac{\alpha a D_0 t}{(k_1 + k_2) b \cdot 20} \right) \bigg/ \log \left( 1 + \frac{\alpha a D_0 t}{(k_1 + k_2) b \cdot 100} \right).$$

$t$  will be constant if the apparatus is unmoved and therefore put  $\delta = at/20b$ .

$$\text{Then } \frac{N_1 - N_2}{N_1} = 1 - \frac{1}{5} \log \left( 1 + \frac{\alpha D_0}{(k_1 + k_2)} \delta \right) \bigg/ \log \left( 1 + \frac{\alpha D_0}{(k_1 + k_2)} \cdot \frac{\delta}{5} \right).$$

First  $(N_1 - N_2)/N_1$  and  $D_0$  are determined at the temperature of the laboratory where both  $\alpha$  and  $k_1 + k_2$  are well known. The constant  $\delta$  can, therefore, be calculated from the equation. The same determination is repeated at the higher temperature and, using the calculated value of  $\delta$ ,  $a/(k_1 + k_2)$  is calculated from the equation. Since this experiment only determines the values of  $\alpha$  relative to its value at the temperature of the laboratory, this last value is taken as unity.

*Apparatus.*—The general arrangement is shown in the accompanying figure. The Röntgen bulb, X, sends a single flash of rays through windows cut in the lead screen, S, and ionises a layer of air between each of the two pairs of electrodes, A and B. Slits placed in front of A and B regulate the thickness of the ionised layer. The pair of electrodes, B, is simply an adjustable standard. It serves to correct for irregularities in the discharge



through the bulb, and to balance or nearly balance the effect in A, so that small differences in charge in A may be determined more accurately. One electrode is maintained at a constant positive potential by means of cells, and the other may be earthed, insulated, or connected to the electrometer. By means of a movable shield some of the rays may be cut off from B, so

that it may be adjusted to exactly balance the effect of A. In order to keep the temperature constant the electrodes are contained in a double-walled vessel through which tap water may circulate.

The pair of electrodes A is the real working pair. One electrode is maintained at any desired negative potential by means of cells, and the other may be earthed, insulated, or connected to the electrometer. The charge received is evidently of opposite sign to that received in B.

The electrodes are contained in a double-walled vessel through which the vapour from a boiling liquid may circulate. In order that the vessel may be used at high temperatures, all the joints are brazed and all the insulation is quartz. In order to vary the sensitiveness of the electrometer at will, A and B have each a variable capacity, C, attached to them. These are air condensers, of which each electrode consists of 10 parallel plates. One electrode may slide up to the other so that the plates are interleaved and the capacity is large, or it may slide quite clear so that the capacity is small. The electrometer is of the Dolezalek pattern, with a fine platinum suspension. As used, the sensitiveness is about 100 whole divisions for 1 volt.

#### *Readings taken.*

I. *Ratio of the Capacities of the System.*—We must first know the ratio between the capacities of the system in the various conditions used.

These conditions are—(a) Variable capacities, C, both open, and A and B connected together to the electrometer. (b) A alone connected to the electrometer with its variable capacity closed. (c) B alone connected to the electrometer with its variable capacity closed.

By putting a stop on the variable capacity connected to B, this third capacity was adjusted to equality with the second, and by sharing a charge on the system with the same Leyden jar, the ratio of the capacity in the case (a) to that in the case (b) or (c) was found to be 0.0694.

II. *Determination of  $(N_1 - N_2)/N_1$  and  $D_0$ .*—One electrode in B is at +80 volts throughout the series of readings.

(a) One electrode in A is at -100 volts, and with the variable capacities open both it and B are connected to the electrometer. The shield in front of B is then adjusted until there is no deflection, when a flash passes through the bulb. This means that the charge received by B is equal and opposite to that received by A when its potential is -100 volts.

(b) A is raised to the highest available negative potential (-370 to -380 volts) and the variable capacities are both closed. A single flash passes in the bulb, and A and B are separately connected to the electrometer. Call the deflection when B is connected the first deflection, and when

A is connected the second deflection. The second deflection evidently gives  $D_0$  if we may assume that there is no recombination with this large field.

(c) A is charged to  $-100$  volts, the capacities are both closed, and the first and second deflections are obtained as in (b). These two deflections should be equal, and each should be proportional to  $N_1$ .

(d) A is still charged to  $100$  volts, and both capacities are closed. After the flash through the bulb, B is connected to the electrometer giving the first deflection. Then without disconnecting B, A is also connected to the electrometer and the capacities are opened. This gives the third deflection, which should be zero if the first adjustment was accurate.

(e) A is charged to  $-20$  volts, and the process in (d) is repeated. The third deflection here is proportional to  $N_1 - N_2$ .

$(N_1 - N_2)/N_1$  will evidently be this  $\frac{\text{third deflection}}{\text{first deflection}} \times 0.0694$ , for the capacity when the third deflection is measured is  $0.0694$  time the capacity when the first deflection is measured.

We thus have  $D_0$ ,  $(N_1 - N_2)/N_1$ ,  $V_2$  and  $V_1$ , and we know  $\alpha$  and  $k_1 + k_2$  at the temperature of the laboratory. We can therefore calculate  $\delta$ .

The series of readings is then completely repeated with A at an arranged higher temperature. At the higher temperature we can calculate  $\alpha/(k_1 + k_2)$ , using the value of  $\delta$  which we have determined.

At some of the higher temperatures  $k_1 + k_2$  has been determined,\* and at these temperatures, therefore, we can calculate  $\alpha$ .

One source of trouble in the experiment is the irregularity of the bulb. In spite of trying several forms of contact breaker and putting a large capacity across the break, the variability was never quite suppressed. Usually the bulb would give a whole series of uniform flashes and then some irregular ones. When the bulb was variable, and the first deflection therefore inconstant, a number of readings was taken under each of the headings (a), (b), (c), (d), (e). The first and second and the first and third deflections were then plotted against one another, and from these curves the values of the second and third deflections for a particular value of the first deflection were read off.

The following is a series of readings taken on April 29, 1908:—

\* P. Phillips, "Ionic Velocities at Different Temperatures," 'Roy. Soc. Proc.,' A, 1906.

Temperature 16° C.

1st deflection.	2nd deflection.	3rd deflection.	E.M.F. in A.
6·39	-6·72	—	360 volts
6·39	-6·39	—	100 „
6·39	—	0	100 „
6·39	—	22·0	20 „

$$D_0 = 6.72, \quad \frac{N_1 - N_2}{N_1} = \frac{22.0}{6.39} \cdot 0.0694 = 0.239.$$

$\alpha$  is taken as unity at 16°.  $k_1 + k_2 = 3.15$  cm. per sec. per volt per cm.

$$\frac{N_1 - N_2}{N_1} = 0.239 = 1 - \frac{1}{5} \log \left( 1 + \frac{\alpha \delta D_0}{k_1 + k_2} \right) / \log \left( 1 + \frac{\alpha \delta D_0}{5(k_1 + k_2)} \right);$$

therefore

$$5(1 - 0.239) = 3.805 = \log \left( 1 + \frac{\alpha \delta D_0}{k_1 + k_2} \right) / \log \left( 1 + \frac{\alpha \delta D_0}{5(k_1 + k_2)} \right).$$

The values of the function  $\log(1 + A) / \log(1 + \frac{1}{5}A)$  were calculated for different values of A and a curve was drawn from these values. The value 3.805 for the function is given by a value 0.99 for A; hence

$$\frac{\alpha \delta D_0}{k_1 + k_2} = 0.99 = \frac{1 \times \delta \times 6.72}{3.15},$$

so that

$$\delta = 0.467.$$

Temperature = 100°, *i.e.* with water in the boiler.

1st deflection.	2nd deflection.	3rd deflection.	E.M.F. in A.
4·82	-4·89	—	370
4·82	-4·82	—	100
4·82	—	0	100
4·82	—	6·70	20

$$\delta = 0.467. \quad D_0 = 4.89. \quad \frac{N_1 - N_2}{N_1} = \frac{6.7 \times 0.0694}{4.82} = 0.0964.$$

$$\text{Thus } 5(1 - 0.0964) = 4.518 = \log \left( 1 + \frac{\alpha \delta D_0}{k_1 + k_2} \right) / \log \left( 1 + \frac{\alpha \delta D_0}{5(k_1 + k_2)} \right);$$

$$\text{whence, from the curve, } \frac{\alpha \delta D_0}{k_1 + k_2} = 0.282,$$

so that

$$\frac{\alpha}{k_1 + k_2} = \frac{0.282}{0.467 \times 4.89} = \underline{\underline{0.1234.}}$$

After a series of readings with water in the boiler, anilin was next used. At first the circulation of the anilin vapour was not fast enough, and the temperature only rose to 155° C. As this remained fairly constant, however, several determinations were made at this temperature.

On employing a larger gas burner the temperature rose to its proper value (176° C.), and readings were taken at this temperature. Finally, the boiler was filled with a naphthalene monobromide, and a temperature of 270°—276° C. was attained. The boiling point of this substance gradually fell on prolonged boiling, due evidently to decomposing a little. In the first determination the temperature was 276° C., and in the last 270° C., and therefore the mean temperature was taken as the temperature throughout.

The following are the values obtained at the different temperatures for  $\alpha/(k_1 + k_2)$  :—

100°.	155°.	176°.	273°.
0·1234	0·0840	0·0734	0·0303
0·1304	0·0880	0·0717	0·0262
0·1276	0·0876	0·0746	0·0317
0·1184	0·0834	0·0744	0·0316
0·1176	0·0856	0·0720	—
Mean... 0·1235	0·0857	0·0732	0·0300

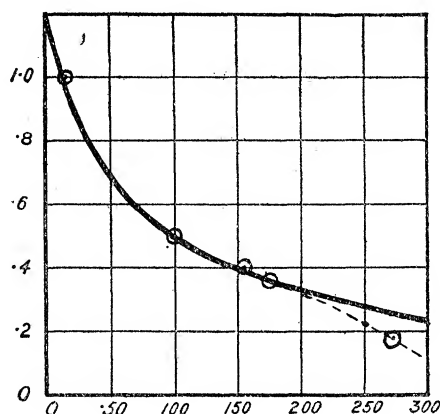
From the curve given in the author's paper mentioned above,  $k_1 + k_2$  at 100° is 4·05. The highest temperature attained in the experiment described in that paper was 138° C., and therefore one must extrapolate in order to get the values of  $k_1 + k_2$  at higher temperatures. These values are at 155° 4·65, at 176° 4·90, and at 273° 5·95.

The first two extrapolations are small, but the last is too large to be safe. Using these values for  $k_1 + k_2$ , we get the following values for  $\alpha$  :—

Temperature, ° C. ....	16	100	155	176	273
$\alpha$ .....	1·0	0·500	0·399	0·360	0·178

Beside the extrapolation being very large for the last temperature, it will be seen later that at this temperature diffusion probably begins to make itself felt, and in consequence 0·178 is probably considerably too low a value. Judging from the curves given below, the author would make a rough estimate that it is about 30 per cent. below its proper value, *i.e.* that  $\alpha$  is about 0·25.

The curve showing the relation between  $\alpha$  and the temperature shows that the recombination decreases somewhat rapidly with rise of temperature, but less rapidly as the temperature rises.



*Note on the Effect of Diffusion.*

L. L. Hendren\* showed experimentally that in the conditions employed by him diffusion was negligible, and judging from his conditions it should also be negligible here.

In order to test this the width of the slit in front of A was reduced, and thus the layer of air ionised was made thinner. Under these conditions diffusion would be more effective and would apparently decrease the value of  $\alpha$ .

$\alpha$  was therefore determined with different widths of slit, and the value of  $\alpha$  was plotted against the width of the slit.

The following values were obtained at 100° C. :—

$\alpha$ .....	0.500	0.505	0.467	0.31
Width of slit .....	1.5	1.0	0.5	0.3

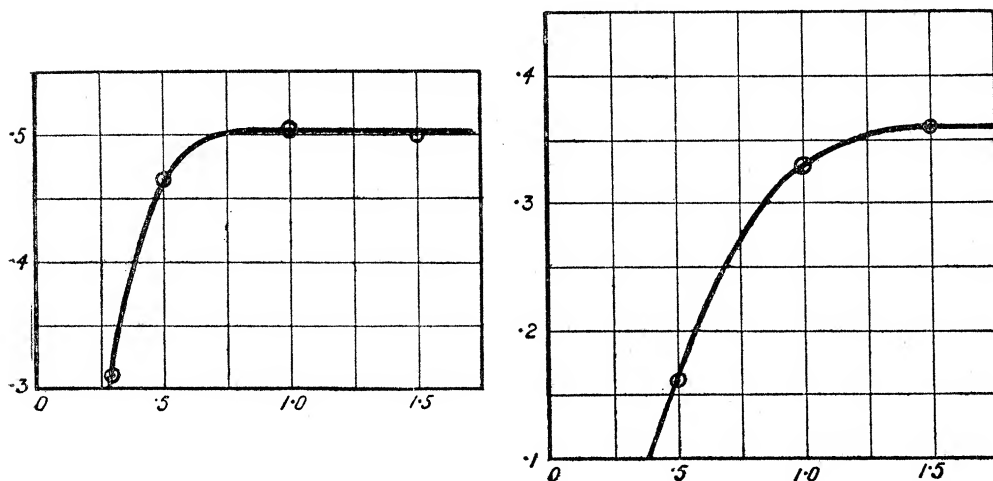
At 176° C.

$\alpha$ .....	0.36	0.33	0.16	Deflections too small for $\alpha$ to be measured
Width of slit .....	1.5	1.0	0.5	0.3

At 273° C. the deflections were so small when the width of the slit was reduced that it was not possible to measure  $\alpha$ , and so the test could not be carried out at this temperature.

\* 'Phys. Review,' November, 1905.

The curves make it evident that at 100° C. we are safely within the limits where diffusion is negligible. At 176° we are evidently just within the limits, and therefore we are probably outside the limits at 273° C., and the value of  $\alpha$  will be too low.



Erikson\* has just published a paper on the same subject as this paper, but he uses an entirely different method. The results, as far as they may be compared, are nearly the same; but the comparison cannot be made accurately, as these experiments were carried out at constant pressure, while his were at constant density.

The variation of  $\alpha$  with density has only been determined at room temperatures, and therefore we cannot correct for the difference in density at the higher temperatures.

If Hendren's results (in the paper before mentioned) could be extended to higher temperatures, *i.e.* if  $\alpha$  varies with the density in the same way at the higher temperatures, then Erikson's value for  $\alpha$  at 100° C. would be 10 per cent. below the value found by this experiment.

It is difficult to estimate what would be the effect of the lack of uniformity of the ionisation in his experiment, but it might account for the difference.

In conclusion, I wish to thank Prof. Trouton and Prof. Porter for their kind encouragement and valuable suggestions during the progress of the experiment which was carried out at University College, and at the same time to acknowledge the Government grant which defrayed the expenses.

\* 'Phil. Mag.,' August, 1909.